POROUS STRUCTURE AND REACTIVITY OF BROWN COAL HUMIC ACIDS CHARS OF DIFFERENT DEGREES OF DEMINERALIZATION

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INTRODUCTION

Humic acids are the main constituent of brown coals and can be regarded as a model substance representing the organic matter of coals of low degree of coalification. Humic acids can be obtained with a much lower mineral matter content than that in the parent coals. They seem to be a suitable material for fundamental studies on pyrolysis and gasification of coals of low rank.

It is troublesome to obtain humic acids in a state of high purity. This research was carried out to evaluate the influence of the degree of demineralization of brown coal humic acids on their behaviour in the processes of carbonization and steam gasification, with particular attention to the development of their capillary structure.

EXPERIMENTAL

A Polish humodetrinitic brown coal (moisture=52.1%,raw; ash=9.5%, dry; carbon=70.8%,dry,ash-free; hydrogen=6.0%,dry,ash-free) was demineralized with dilute HCl. The demineralized brown coal contained 5.8,dry, of ash. Humic acids (HA) were obtained from this coal by alkaline extraction with 1% NaOH followed by precipitation with dilute HCl. The obtained HA gel contained 1.4%,dry, of ash. Further demineralization with HCl and mixtures of HCl and HF permitted to obtain HA with following ash contents (A^{d}_{HA}%,dry): 0.4, 0.18 and 0.07%. The obtained HA were designed, respectively, as $HA_{1.4}$, $HA_{0.4}$, $HA_{0.18}$ and $HA_{0.07}$. To the $HA_{0.18}$ gel calcium acetate was added to introduce 1 mmol of Ca per 1 g of organic substance of this HA. The obtained sample was designed as $HA_{0.18}$(Ca). The above mentioned HA were carbonized in a thermogravimetric apparatus (TG) at a heating rate of 5°C/min, in a stream of argon, to the desired heat treatment temperature (HTT). Example of designation of chars: $HA_{1.4}$ carbonized to HTT 900°C was designed as $HA_{1.4}$900. The gasification of chars was carried out in the same TG apparatus in one heating run, to obtain a burn-off of 50%, dry,ash-free. Sorption measurements of benzene and carbon dioxide at 25 were carried out using a gravimetric vacuum apparatus (McBain springs).

An additional suite of $HA_{1.4}$ and $HA_{1.4}$(Ca) samples (1), carbonized to HTT of 800°, 900° and 1100°C, at two heating runs, was included into the sorption measurements.

RESULTS AND DISCUSSION

TG measurements of the HA differing in ash content from 1.4 to 0.07%, indicate a close similarity in the course of their carbonization (loss of mass versus HTT). However, significant differences were observed during gasification of their chars (Figure 1, Table I). This is accompanied by profound differences in the shapes of respective iso-

therms of benzene sorption on the gasified chars (Figure 2) and the slopes of the derived γ -plots (2) shown in Figure 3, analogical in their meaning to the frequently presented α-plots or t-plots(3).

Figure 4 illustrates, for the $HA_{1.4}$...$HA_{0.07}$ and their carbonized and gasified at 900°C chars, the changes in the respective capillary structures caused by demineralization. The influence of lowering of ash content is visible already on the level of the initial HA: a successive decrease of the micropore volume can be noted. This tendency is more accentuated for the non-gasified chars. On gasification, the influence of demineralization with regard to micropores becomes reversed: chars with lowest ash content indicate the highest development of micropore volumes.

The addition of Ca to $HA_{0.18}$ caused an important increase in the rate of gasification and reactivities of the chars (Figure 5, Table I), although the carbon dioxide accessible micropore volumes (V^{DR}_{oCO2}) of the chars, corresponding to different HTTs ,calculated according to the Dubinin-Radushkevich (DR) equation (4), were not very much influenced (Figure 6). It was only for the gasified chars that the influence of calcium on the capillary structure became visible (Figures 7-9, Table I).Catalytic gasification, occuring in the proximity of the calcium compounds ($CaCO_3$ or CaO), favours the development of mesoporosity.

This phenomenon is also clearly visible in case of a different suite of TG gasified chars from $HA_{1.4}$, carbonized previously in a laboratory furnace (two heating runs). The reactivities R^{daf} of these chars, presented in Table II, have been already published (1). As can be noted in Figure 10, the addition of Ca caused, in all cases, a very distinct increase of mesoporosity and a decrease of the micropore volume. A further influence of Ca addition is manifested by diminishing the differences between the capillary structures of the gasified chars from different HTTs (lower part of Figure 10), strongly pronounced in case of the gasified chars without Ca addition (upper part of Figure 10).

An attempt was made to recalculate the reactivities related to 1g of the gasified chars into reactivities related to 1 m^2 of the surface area S_t of these chars. The values of R^{daf}/S_t^{daf} of samples 1-8 in Table I, mark more strongly the influence of demineralization of the HA then do the respective values of R^{daf}. Comparing, in Table II, the values of R^{daf}/S_t^{daf} for samples gasified at the same temperatures but corresponding to different HTTs (e.g. sample 12 with 13 or sample 14 with 18) , it seems that the calculated values of S_t for samples corresponding to higher HTTs are too low (or those corresponding to lower HTTs too high) in relation to the surface areas really partaking in the reaction of gasification (because the respective values of R^{daf}/S_t^{daf} increase with increasing HTT, what does not seem probable).

The values of S_t were calculated as the sum of the surface area of the mesopores (S^{γ}_{mes} calculated from the slopes of the γ-plots) and the geometrical surface area of the micropores. It seems that in case of gasification, it is rather the geometrical surface area of the micropores which should be considered, than their effective (5) surface area (S_{eff} - amount of adsorbate filling volumetrically the micropores, expressed in a formal manner in terms of surface area, representative for the sorptive properties of chars).

These geometrical surface areas of micropores were calculated from the micropore volumes, assuming their slit-like shape (6). In case of all chars without Ca addition, the micropore volumes and the characteristic energies of adsorption E_o (to enable the calculation of χ -the half widths of the slits) were taken from the DR equation. For all chars with Ca addition, the micropore volumes were assumed to be equal to V_o^{γ} from the γ-plots (in Tables I and II, the values of V_{mic} - calculated on the basis of the Gurvitsch rule and the size distribution of the mesopores - V_o^{DR} and V_o^{γ} do not differ significantly) and the values of χ were taken, arbitrary, as 0.5 nm, because the application of the DR equation appeared impossible. For these chars the correction of the experimental isotherms for adsorption in the mesopores (based on a standard benzene isotherm on a non-porous carbon black: Spheron 6-2700) rendered ,not a horizontal, but a decreasing line of the corrected isotherm. This phenomenon was reflected in the γ-plots, an example of which is shown in Figure 8. In the region of lower relative pressures, the experimental points, which usually deviate downwards from the straight line (the micropore filling is not yet completed), are, in case of samples with Ca addition, placed near, or even above, this line. This might point to an enhanced specific adsorption of benzene on the chars with Ca addition.

CONCLUSIONS

1. Successive demineralization of the HA from ash content of 1.4% to 0.4, 0.18 and 0.07%, lowered the reactivity R^{daf} of the HA900 chars at steam gasification: at 800°C by a factor of 6,and at 900°C by a factor of about 3.5. For chars from $HA_{0.18}$ and $HA_{0.07}$ the reactivities were almost identical. In this range of gasification temperatures the energy of activation for the chars from $HA_{1.4}$ was 110 kJ/mol and increased for the more demineralized chars to about 170-180 kJ/mol, with respective frequency factors of the order of 10^5 and 10^8 g/g.h.

2. As a result of demineralization, in the capillary structure of the steam gasified chars (e.g. at 800°C), a successive increase of the volume of benzene accessible micropores is noted, from c.0.15 to c.0.4 cm^3/g. This is accompanied by a decrease of the volume of mesopores from c.0.5 to below 0.1 cm^3/g. The respective effective benzene surface areas S_{eff} increase from 700 to 1400 m^2/g.

3. The strong increase of reactivity of the demineralized HA chars after Ca addition (a 30-fold increase of reactivity was observed after addition of 1 mmol to 1 g of $HA_{0.18}$) was accompanied by a very strong development of the volume of mesopores, with the volume of micropores becoming very small .

4.For the gasified chars obtained from HA with Ca addition, an enhanced adsorption of benzene at low relative pressures was observed. As a result, the evaluation of microporosity using the Dubinin approach was impossible. In these cases the application of the α-plots (γ-plots) appeared very useful.

ACKNOWLEDGEMENTS

This work was sponsored by the Polish Academy of Sciences (Scientific Program CPBP 0.1 16).

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Table I. Steam gasified HA900 and HA(Ca)900 chars (one heating run)

Sample No	A_{HA} % dry	Gasif. at: °C	Based on benzene adsorption: V_{mic} cm³/g	V^{γ}_{o} cm³/g	V^{DR}_{o} cm³/g	E_o kJ/mol	S^{γ}_{mes} m²/g	S_{eff} m²/g	S_t m²/g	R^{daf} g/g.h	R^{daf}/S^{daf}_t g/m².h·10³
			Chars from HA								
1	1.4	800	0.159	0.172	0.146	24.0	290	723	582	1.98	3.21
2	0.4	800	0.388	0.424	0.410	17.7	131	1346	704	0.40	0.56
3	0.18	800	0.431	0.463	0.450	19.2	68	1401	756	0.38	0.50
4	0.07	800	0.442	0.452	0.459	21.8	51	1411	865	0.34	0.39
5	1.4	900	0.179	0.172	0.147	36.5	236	672	671	5.72	8.06
6	0.4	900	0.268	0.294	0.246	19.7	187	916	574	2.28	3.91
7	0.18	900	0.360	0.385	0.351	19.5	117	1157	664	2.04	3.05
8	0.07	900	0.399	0.433	0.437	19.2	53	1348	721	1.66	2.30
			Chars from HA(Ca)								
9	0.18	660	0.124	0.100	-	-	279	575	479	0.68	1.10
10	0.18	700	0.074	0.075	-	-	285	507	435	1.60	2.81
11	0.18	800	0.064	0.023	-	-	209	277	255	5.22	15.60

Table II Steam gasified chars from $HA_{1.4}$ and $HA_{1.4}(Ca)$ (two heating runs)

Sample No	HTT °C	Gasif. at: °C	Based on benzene adsorption: V_{mic} cm³/g	V^{γ}_{o} cm³/g	V^{DR}_{o} cm³/g	E_o kJ/mol	S^{γ}_{mes} m²/g	S_{eff} m²/g	S_t m²/g	R^{daf} g/g.h	R^{daf}/S^{daf}_t g/m².h·10³
			Chars from $HA_{1.4}$								
12	800	800	0.281	0.274	0.251	32.2	215	959	959	0.84	0.83
13	800	800	0.200	0.188	0.178	18.1	176	703	431	0.71	1.56
14	900	850	0.202	0.211	0.195	19.1	141	719	437	1.50	3.43
15	900	900	0.187	0.194	0.179	17.5	127	657	374	2.64	7.06
16	1100	850	0.044	0.028	0.026	17.3	70	147	105	0.85	8.10
17	1100	900	0.054	0.052	0.054	13.2	40	200	95	1.39	14.60
			Chars from $HA_{1.4}(Ca)$								
18	800	800	0.064	0.032	-	-	262	357	326	3.12	7.68
19	900	725	0.077	0.021	-	-	358	420	400	0.54	1.03
20	900	750	0.076	0.041	-	-	294	415	376	1.08	2.20
21	900	800	0.049	0.005	-	-	316	331	326	1.92	4.42
22	1100	800	0.037	0.016	-	-	251	298	283	1.38	3.70
23	1100	850	0.037	0.028	-	-	218	301	274	2.16	6.00
24	1100	900	0.045	0.002	-	-	270	276	274	3.00	8.24

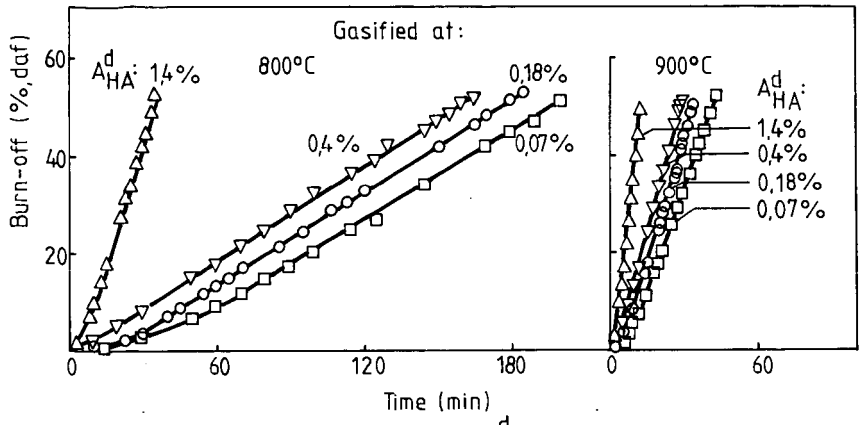

Figure 1. Infuence of ash (%, dry) in initial HA - A^d_{HA} on the course of steam gasification of the HA900 chars.

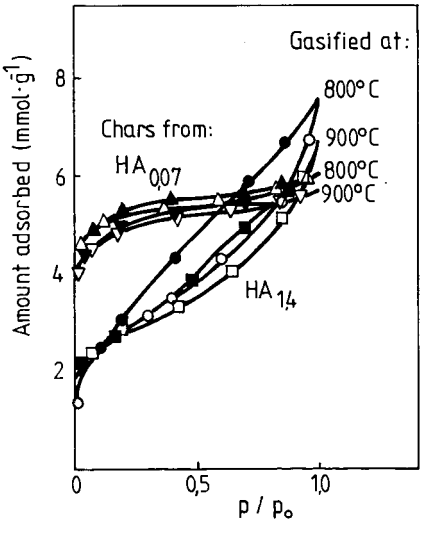

Figure 2. Changes in the shape of isotherms of benzene sorption (25°C) on steam gasified (burn-off 50%, daf) HA900 chars, caused by demineralization of the HA.

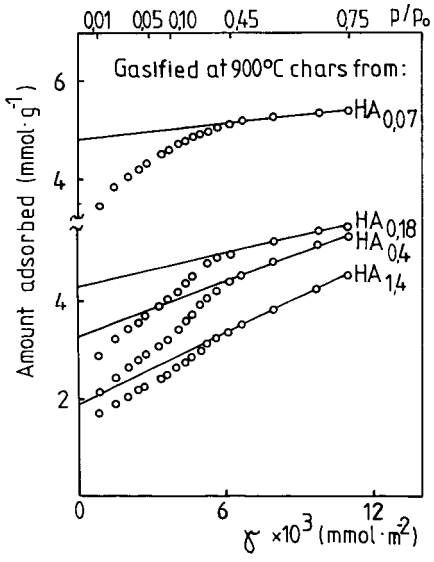

Figure 3. γ-plots for benzene adsorption (25°C) on steam gasified (burn-off 50%, daf) HA900 chars obtained from HA of different degrees of demineralization.

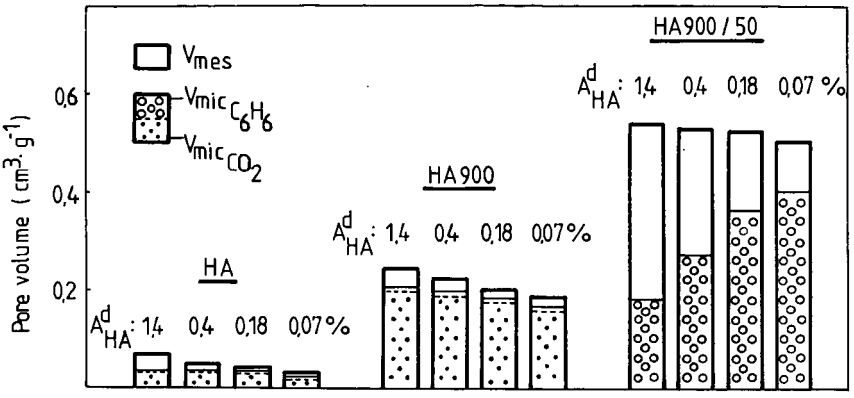

Figure 4. Influence of A^d_{HA} (%, dry) on the development of porosity in humic acids: initial (HA), carbonized (HA900) and steam gasified at 900°C to 50% burn-off, daf (HA900/50).

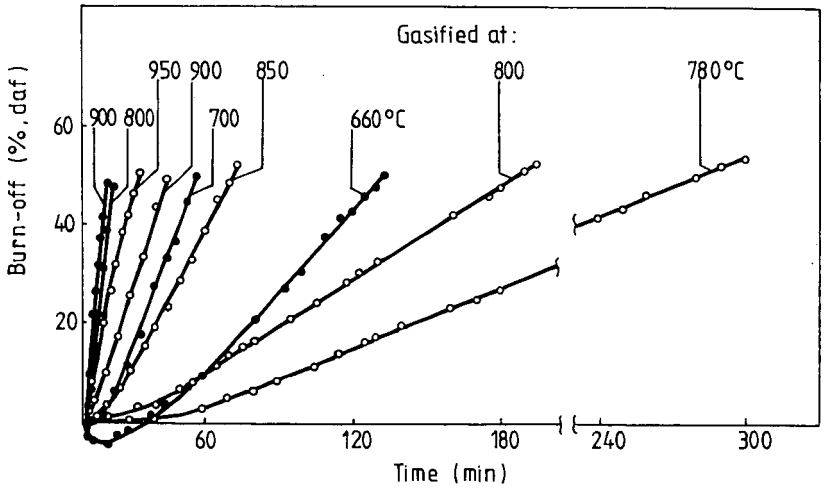

Figure 5. Course of steam gasification of the $HA^{900}_{0,18}$ chars (∘) and $HA(Ca)^{900}_{0,18}$ chars (•).

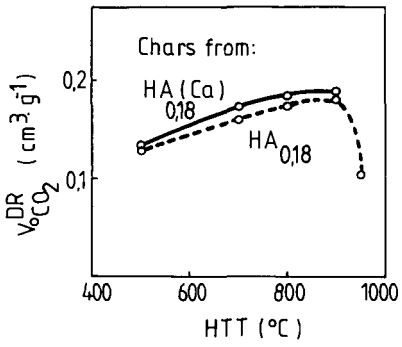

Figure 6. Variations of $V_{\infty CO_2}^{DR}$ during carbonization of $HA_{0,18}$ and $HA_{0,18}$ (Ca).

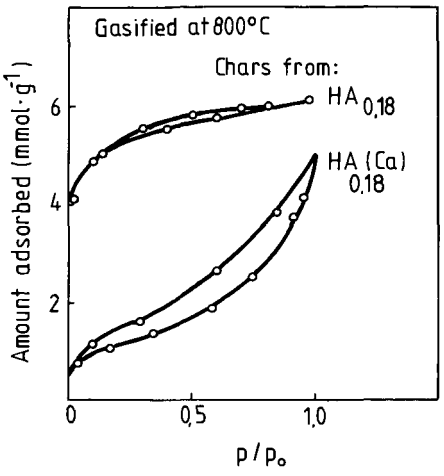

Figure 7. Isotherms of benzene sorption (25°C) on steam gasified (burn-off 50%, daf) $HA_{0,18}900$ and $HA_{0,18}$ (Ca) 900 chars.

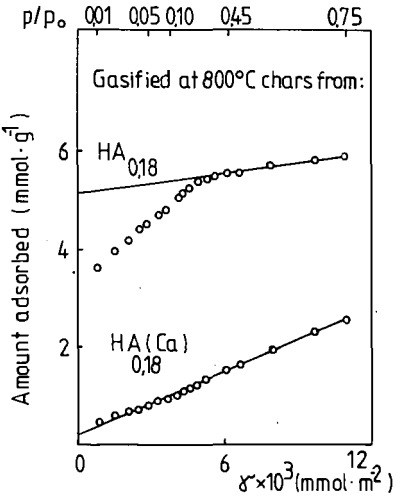

Figure 8. γ-plots for benzene adsorption (25°C) on steam gasified (burn-off 50%, daf) $HA_{0,18}900$ and $HA_{0,18}$ (Ca) 900 chars.

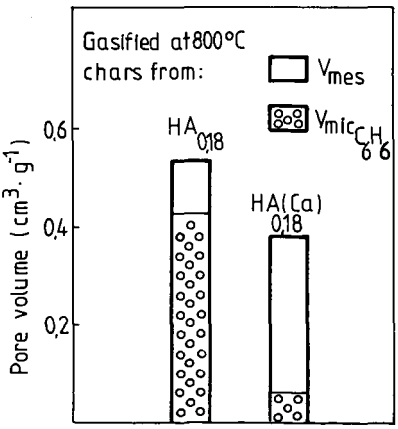

Figure 9. Decrease in microporosity and increase in mesoporosity of steam gasified (burn-off 50%, daf) chars (HTT 900°C), caused by Ca addition to $HA_{0,18}$.

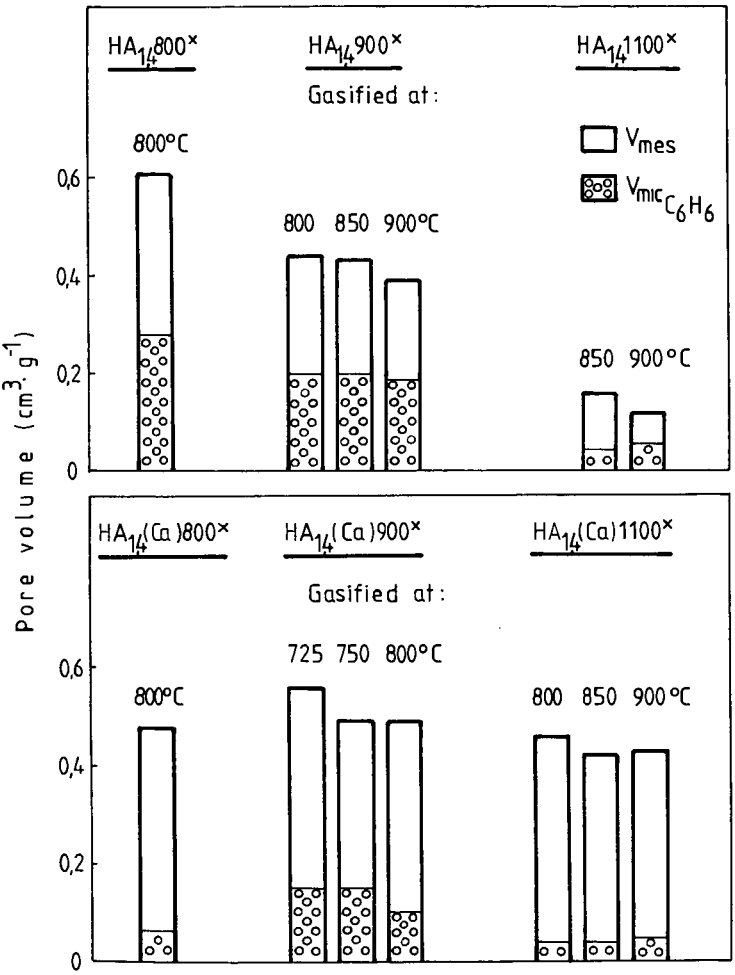

Figure 10. Development of porosity in steam gasified (burn-off 50%, daf) chars obtained from HA_{14} and $HA_{14}(Ca)$.
×) Carbonization was carried out at two heating runs.